A further study of crystallization of lithium perchlorate from LiClO$_4$-NaCl-H$_2$O system

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The aim of this paper is to define feasible process pathways of fractional crystallization of NaCl and LiClO$_4$-3H$_2$O from LiClO$_4$-NaCl-H$_2$O system using the information on the equilibrium of the LiClO$_4$-NaCl-H$_2$O system at different temperatures, as well as the information on the composition of the starting solution obtained by electrolysis and double exchange with LiCl.

The paper also synthesizes a feasible process structure that can be applied for the process of fractional crystallization, and gives a simulation of the process by calculating the material balance of the process. The parameters of relevant process paths that were obtained prove that the process presented in this paper is feasible in practice and applicable in industry.

Keywords: Lithium-perchlorate, equilibrium, processing pathway.

Introduction

Lithium perchlorate (LiClO$_4$) is typically used as an oxidant in the manufacture of rocket fuels due to the fact that it contains around 60% (w/w) of oxygen, which is the highest oxygen weight ratio among the all known perchlorates.

A large scale application of lithium perchlorate nowadays also refers, however, to lithium ion batteries characterized by excellent energy performances. The lithium electrochemical properties such as the specific electric energy consumption (electrochemical equivalent) of 3.86 Ah/g or 13.9 kC/g, the standard electrode potential of -3.045V, as well as the extraordinary movability of Li$^+$ ions, which is the highest of all known, define LiClO$_4$ as one of the most concentrated sources of electric energy currently available.

Thanks to this property, lithium batteries are nowadays used for various electronic machines. One of the most promising potential applications of lithium perchlorate is in the manufacture of chemical sources of energy (i.e. fuel cells) for electric cars. Apart from that, this compound is finding even more significant role in the organic synthesis, having been discovered in the past decade as an homogenous catalyst for many important organic reactions such as Friedel-Crafts acylation, Diels-Alder reactions, etc.

The production of lithium perchlorate described in this paper involves the following two stages (Schumacher, 1960):

1. electrochemical oxidation of sodium-chlorate to sodium-perchlorate:
   \[ \text{NaClO}_3 + \text{H}_2\text{O} \rightarrow \text{NaClO}_4 + \text{H}_2 \uparrow \]

2. conversion of NaClO$_4$ into LiClO$_4$ according to the reaction:
   \[ \text{NaClO}_4 + \text{LiCl} \rightarrow \text{LiClO}_4 + \text{NaCl} \]

This work includes a detailed analysis of the equilibrium in the system of LiClO$_4$-NaCl-H$_2$O; based on this equilibrium, feasible process pathways of lithium perchlorate crystallization are defined, feasible process structure is synthesized and basic parameters of the process are calculated by balancing the system.
The research into the process of crystallization in the system of LiClO₄-NaCl-H₂O

The equilibrium in the system of LiClO₄-NaCl-H₂O is shown in the equilibrium diagram in Figure 1 based on the facts on solubility given in Table 1. It refers to the range of temperatures between 2 °C and 80 °C.

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Grams/Grams Solution</th>
<th>Solid Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>LiClO₄</td>
<td>NaCl</td>
</tr>
<tr>
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<td>0.2640</td>
</tr>
<tr>
<td></td>
<td>0.1932</td>
<td>0.1711</td>
</tr>
<tr>
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<td>0.2902</td>
<td>0.1281</td>
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<tr>
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<td></td>
<td>0.3595</td>
<td>0.0000</td>
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<tr>
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<td>0.0000</td>
<td>0.2667</td>
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<tr>
<td></td>
<td>0.2780</td>
<td>0.1368</td>
</tr>
<tr>
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<td>0.3662</td>
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<td>0.3751</td>
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<td>60</td>
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<td></td>
<td>0.4840</td>
<td>0.0000</td>
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<td>80</td>
<td>0.0000</td>
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<tr>
<td></td>
<td>0.1910</td>
<td>0.1831</td>
</tr>
<tr>
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<tr>
<td></td>
<td>0.4797</td>
<td>0.0748</td>
</tr>
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<td>0.5365</td>
<td>0.0615</td>
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<tr>
<td></td>
<td>0.5384</td>
<td>0.0448</td>
</tr>
<tr>
<td></td>
<td>0.5450</td>
<td>0.0237</td>
</tr>
<tr>
<td></td>
<td>0.5579</td>
<td>0.0000</td>
</tr>
</tbody>
</table>

By the electrolysis of sodium chlorate, sodium perchlorate is obtained; double exchange with LiCl results in the solution defined as the system of LiClO₄-NaCl-H₂O. The concentration ratio of lithium perchlorate and sodium chloride is constant and amounts to 1.82 (Schumacher, 1960; Jotanovic and Andric, 2010).

Therefore, depending on the concentration of sodium perchlorate that can be achieved in the process of electrolysis (600–1000 g/l NaClO₄), different concentrations of LiClO₄ and NaCl can be obtained; however they always lie on the 0-X vector of the equilibrium diagram, Figure 2.
A further study of crystallization of lithium perchlorate from LiClO₄-NaCl-H₂O system

FIGURE 1. EQUILIBRIUM IN THE SYSTEM OF LiClO₄-NaCl-H₂O

Source: The graph was constructed from data from “The Perchlorates” by Schumacher (1960, p.233).

FIGURE 2. BASIC CRYSTALLIZATION AND SEPARATION, LiClO₄ or NaCl
The observation of crystallization area of certain salts in the equilibrium diagram leads to the conclusion that, considering the concentration of LiClO₄ and NaCl in the system of LiClO₄-NaCl-H₂O, the points 1', 1"..., which characterize the concentration of salts in the system, lie in NaCl crystallization area. This is very important for determining the process paths and process structure of the crystallization of lithium perchlorate from this system.

If we consider the equilibrium of the LiClO₄-NaCl-H₂O system as well as the facts that were previously established and which refer to the concentration of the system of LiClO₄-NaCl-H₂O as the starting point for the crystallization of lithium perchlorate, we conclude that the process of crystallization should be performed at two isotherms at the minimum. The upper isotherm should not be at the excess of 95 °C, since the aim is to produce LiClO₄·3H₂O (lithium perchlorate trihydrate) which releases its crystal water at 95 °C.

The isotherms of 20 °C and 80 °C were adopted for the purpose of the analysis of process paths for the crystallization in this system. The parameters of the solution that represents the system of LiClO₄-NaCl-H₂O, which undergoes crystallization of salts, are determined by the following:
- the content of LiClO₄;
- the content of NaCl;
- temperature;
- flow.

**FIGURE 3. FEASIBLE PATHWAY DIAGRAM FOR SYSTEM LiClO₄-NaCl-H₂O**
Synthesis of Crystallization-Based Separation Systems has been the subject of research of many authors (e.g. see Nyvlt et al., 1985; Hamiski, 1979; Cisternas and Swaney, 1988; Cisternas and Rudd, 1993) and it mainly includes the following:

- Crystallization design problem overview;
- Fractional crystallization;
- Fractional crystallization with heat integration.

The authors of this paper have investigated possible crystallization pathways of lithium perchlorate from the previously defined system of LiClO$_4$-NaCl-H$_2$O. Feasible pathway diagram is shown in Figure 3. The multicomponent electrolytic system of LiClO$_4$-NaCl-H$_2$O is separated into lithium perchlorate trihydrate and sodium chloride by means of fractional crystallization. The process pathway includes the following elementary steps:

- The starting flow with the content of 0.2550 mass portion of LiClO$_4$ and 0.1470 mass portion of NaCl (point 1 in the diagram) is mixed with the flow of mother solution from the system for the crystallization of lithium chloride trihydrate;
- The mixed flow (point 2 in the diagram) is directed to the isothermic crystallizer of sodium chloride in which the process finishes at the final temperature of 80$^\circ$C;
- The producing flow of the suspension from the crystallizer separates into crystal sodium chloride and the flow of mother solution which, in the form of a eutonic system(point 4 in the diagram), is directed into the cooler crystallizer- isohydric crystallization of lithium perchlorate trihydrate;
- Cooling of the system and isohydric crystallization of LiClO$_4$·3H$_2$O are performed in the crystallizer. The final temperature of cooling of the system ranges between 10 $^\circ$C and 20 $^\circ$C;
- The production flow of the suspension from the crystallizer is separated into crystal lithium perchlorate trihydrate and the flow of mother solution (point 5 in the diagram) which is directed to the beginning of the process to be mixed with the starting solution.

The process pathway of fractional crystallization of salts from the system of LiClO$_4$-NaCl-H$_2$O defined in this way leads to creation of the following process/state structure shown in Figure 4.

The basic elements of the plant are the isothermal crystallizer (I) with outside forced circulation of the solution and the cooler crystallizer with contact surface cooling (II). Both apparatuses, as well as other apparatuses that are component parts of this plant, are nowadays technically improved and their design is supported by relevant knowledge and skills.

The analysis of the process of fractional crystallization, primarily that of lithium perchlorate trihydrate, from the system of NaCl-LiClO$_4$-H$_2$O, which is shown in the feasible process structure (Figure 4), was performed based on the results of the material balance simulation of the total process system.

This process structure is the sum of the subsystem of sodium chloride crystallization and the subsystem of lithium perchlorate trihydrate crystallization. Simulation model of material balance is the system of the following equations:

\[
\begin{align*}
    f_1 & : \ m_1 + m_7 = m_2 \\
    f_2 & : \ m_1 \cdot c_1^{(1)} + m_7 \cdot c_1^{(7)} = m_2 \cdot c_1^{(2)} \\
    f_3 & : \ m_1 \cdot c_2^{(1)} + m_7 \cdot c_2^{(7)} = m_2 \cdot c_2^{(2)} \\
    f_4 & : \ m_2 = m_4 + m_5 + m_8
\end{align*}
\]
Before solving the system of balance equations, it is necessary to determine the composition of the flow of mother solution that leaves the isothermal crystallizer (I) and feeds the cooler crystallizer (II) as such. The composition of this flow is determined by the
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point 4 in the equilibrium diagram of the system of LiClO$_4$-NaCl-H$_2$O and it is a eutonic composition (Figure 3).

It should be emphasized that the composition of mother solution that leaves the cooler crystallizer is also determined by the content of sodium chloride and lithium perchlorate. The composition of this solution (point 5 in Figure 4) is determined by the point that represents the cross-section of the line drawn from the peak of the triangle where the content of LiClO$_4$ is $c_2 = 1$ and the isotherm $t = 20^\circ$C.

Now we can finally define the parameters that should be specified as numbers in order to solve the system of balance equations. The given parameters are as follows:

\[
\begin{align*}
m_1 &= 1000 \text{ kg/h} \\
c_1^{(5)} &= 0.0615 \\
c_1^{(i)} &= 0.1470 \\
c_2^{(5)} &= 0.5365 \\
c_2^{(i)} &= 0.2550 \\
c_2^{(7)} &= 0.3100 \\
c_2^{(9)} &= \frac{M_{\text{LiClO}_4}}{M_{\text{LiClO}_4 \cdot 3H_2O}} = \frac{106.5}{160.5} = 0.6635
\end{align*}
\]

Concentration mark: 1- NaCl, 2- LiClO$_4$.

The results of the simulation of the process structure of fractional crystallization of salts from the system of LiClO$_4$-NaCl-H$_2$O shown in Figure 4 are given in the Table 2.

### TABLE 2. PROCESS STRUCTURE SIMULATION RESULTS

<table>
<thead>
<tr>
<th>Flow</th>
<th>1</th>
<th>2</th>
<th>4</th>
<th>5</th>
<th>7</th>
<th>8</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow rate, m kg/h</td>
<td>1000</td>
<td>1215.45</td>
<td>468.65</td>
<td>599.79</td>
<td>215.45</td>
<td>147</td>
<td>384.25</td>
</tr>
<tr>
<td>NaCl, $c_1$ (mass portions)</td>
<td>0.1470</td>
<td>0.1512</td>
<td>0</td>
<td>0.0615</td>
<td>0.1712</td>
<td>1.0</td>
<td>0</td>
</tr>
<tr>
<td>LiClO$_4$, $c_2$ (mass portions)</td>
<td>0.2550</td>
<td>0.2647</td>
<td>0</td>
<td>0.5365</td>
<td>0.3100</td>
<td>-</td>
<td>0.6635</td>
</tr>
</tbody>
</table>

Calculation of material balance of the process of fractional crystallization from the system of LiClO$_4$-NaCl-H$_2$O represented by the process structure in Figure 4, and whose results are given in Table 2, proves that the process synthetized in this way is feasible in practice. Process structure simulation for this process is thus concluded.

### Conclusion

The aim of this paper is to give certain contribution to research and defining of the process of fractional crystallization of NaCl and LiClO$_4$ from the system of LiClO$_4$-NaCl-H$_2$O.

Based on consideration of the equilibrium in the system of LiClO$_4$-NaCl-H$_2$O and the content of NaCl and LiClO$_4$ in the starting solution, which is formed by the electrolysis of sodium chlorate and by adding LiCl, the basic feasible process pathway of the process was determined. It includes the following.

- isothermic crystallization of NaCl at 80 $^\circ$C;
- isohydric crystallization (crystallization by cooling) of LiClO$_4$-NaCl-H$_2$O.

Feasible process structure, in which the defined process of fractional crystallization is performed, consists of the two important apparatuses: an isothermal crystallizer (I) and a
cooler crystallizer through contact surface (II), together with other apparatuses and devices that are component parts of the plant.

Process structure simulation, performed by calculating parameters of relevant process flows, has shown that the process is feasible and applicable in industrial practice.

References


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